

# EFFECT OF IONIC ORDERING IN CONDUCTIVITY EXPERIMENTS OF DNA AQUEOUS SOLUTIONS

O.O. LIUBYSH<sup>1</sup>, O.M. ALEKSEEV<sup>1</sup>, S.Yu. TKACHOV<sup>1</sup>,  
S.M. PEREPELYTSYA<sup>2</sup>

<sup>1</sup>Taras Shevchenko National University of Kyiv,  
64, Volodymyrska Str., Kyiv 01033, Ukraine

<sup>2</sup>Bogolyubov Institute for Theoretical Physics, NAS of Ukraine,  
14-b Metrolohichna Str., Kiev, 03680, Ukraine  
perepelytsya@bitp.kiev.ua

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## Abstract

The effects of ionic ordering in DNA water solutions are studied by conductivity experiments. The conductivity measurements are performed for the solutions of DNA with KCl salt in the temperature range from 28 to 70 °C. Salt concentration vary from 0 to 2 M. The conductivity of solutions without DNA but with the same concentration of KCl salt are also performed. The results show that in case of salt free solution of DNA the melting process of the double helix is observed, while in case of DNA solution with added salt the macromolecule denaturation is not featured. For salt concentrations lower than some critical one (0.4 M) the conductivity of DNA solution is higher than the conductivity of KCl water solution without DNA. Starting from the critical concentration the conductivity of KCl solution is higher than the conductivity of DNA solution with added salt. For description of the experimental data phenomenological model is elaborated basing on electrolyte theory. In framework of the developed model a mechanism of counterion ordering is introduced. According to this mechanism under the low salt concentrations electrical conductivity of the system is caused by counterions of DNA ion-hydrate shell. Increasing the amount of salt to the critical concentration counterions condense on DNA polyanion. Further increase of salt concentration leads to the formation of DNA-salt complexes that decreases the conductivity of the system.

## 1 Introduction

DNA double helix is a strong polyelectrolyte which in aqueous solutions dissociates into macromolecular polyanion and mobile cations (counterions) [1,2]. Under the natural conditions the counterions are positively charged metal ions (usually  $\text{Na}^+$  or  $\text{K}^+$ ) that neutralize negatively charged phosphate groups of macromolecule backbone. The counterions and water molecules form an ion-hydrate shell around DNA stabilizing the structure of the double helix [3–8]. In spite of significant mobility of counterions they are organized as the dynamical structure around

macromolecule. This structure may be rather regular due to the homogeneity of DNA backbone [9, 10]. The ordering of counterions around DNA macromolecule determines the elastic properties of the double helix (bending, twisting, denaturation), DNA interaction with biologically active compounds (proteins, drugs), and compaction mechanisms of macromolecule in small volumes (chromosomes, viral capsids) [11–16]. The study of dynamical ordering of DNA counterions is of paramount importance for understanding the mechanisms of DNA biological functioning.

Effects of dynamical ordering of counterions around DNA double helix may become apparent in conductivity experiments due to the interaction of charged particles of the solution with the electric field. As known the electric current in DNA water solutions is caused by the motion of counterions and DNA macromolecules [17–23]. In case of DNA solutions without added salt (salt free solution) the conductivity increases as the concentration of DNA increases because of counterion dynamics in the ion-hydrate shell of macromolecule [17, 18]. Heating the system the conductivity gradually increases, and under the temperatures of the double helix melting there is a sudden change of conductivity that is caused by intensive ejection of counterions from DNA ion-hydrate shell [18]. In case of DNA solution with added salt the conductivity of the system depends on the both counterion type and salt concentration [17, 18]. The dependence on counterion type is caused by different electrophoretic mobility of ions mostly [17], while the dependence on salt concentration may reflect the ordering of the ions in solution. The experimental data show that under the low concentration of added NaCl salt the conductivity of DNA solution is higher than the conductivity of NaCl electrolyte solution, but starting from some defined concentration the conductivity of DNA solution becomes lower than the conductivity of electrolyte [19]. The reason of such concentration dependence of conductivity of DNA solutions is not determined yet.

To elucidate the microscopic picture of conductivity process in DNA solution the phenomenological approaches have been developed, and atom-atom calculations have been performed [24–27]. The results have been showed that the dynamics of counterions in close vicinity to DNA surface is modulated by the charged atomic groups of the double helix backbone. Part of the time counterions spend in complex with DNA (about 1 ns) and another part in free state [28–31]. Free counterions determine the conductivity of DNA solution in many respects that has been taken into consideration in phenomenological models [24, 26]. In the same time, the counterions, tethered to the phosphate groups, form ordered dynamical structure along DNA backbone that may be considered as the lattice of ionic type (ion-phosphate lattice) [9, 10]. The existence of the ion-phosphate lattice is confirmed by observing the modes of ion-phosphate vibrations in the low-frequency Raman spectra of DNA ( $< 200 \text{ cm}^{-1}$ ) [32–35]. The ordering of counterions around the double helix and the formation of the ion-phosphate lattice should affect the conductivity of DNA water solutions.

The goal of the present work is to study the manifestations of counterion ordering around DNA double helix in conductivity experiments of DNA water solutions with added salt. To solve this problem the conductivity of DNA water solutions with KCl salt is studied experimentally in the Section 2. As the result the concentration dependence ( $0 \div 2\text{M}$ ) of conductivity of DNA solutions is obtained at temperature range from 28 to 70 °C (Section 3). For the interpretation of experimental data the phenomenological model is developed basing on electrolyte theory (Section 4). In the Section 5 possible mechanism of ionic ordering around DNA double helix is discussed.

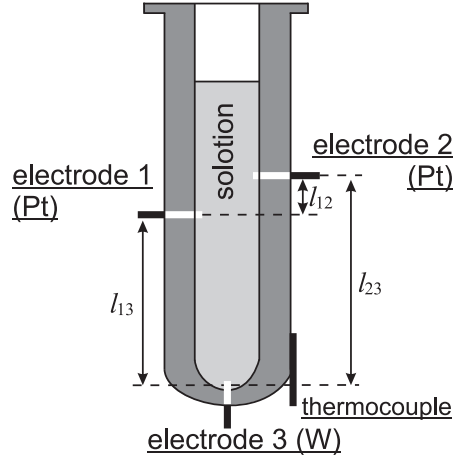


Figure 1: Scheme of the experimental capillary cell.

## 2 Materials and Methods

The samples have been prepared using sodium salt of DNA from salmon testes purchased from Sigma-Aldrich Company (product number D1626). The average length of DNA macromolecules is about 2000 base pairs [36]. To prepare the samples of DNA water solutions the powder of DNA has been diluted in deionized water to the concentration 10 mg/ml. To decrease the viscosity of DNA solution it has been treated by the laboratory automatic mixer and than cooled to the 0 °C without freezing of water. Than the initial solution has been diluted to 2 mg/ml concentration of DNA, and KCl salt has been added to this solution. The concentrations of added salt in the obtained solutions are as follows: 0.4, 0.8, 1.2, 1.6, and 2 M. Water solutions without DNA but with the same concentrations of KCl salt have been also prepared. As the result two series of the samples have been prepared: KCl electrolyte solutions, and water solutions of DNA with KCl salt.

To measure the resistance of the sample the solution (about 0.3 ml) is poured into cylindrical capillary made of quartz glass with two platinum electrodes (electrode 1 and electrode 2) and one wolfram electrode (electrode 3) incorporated into the capillary walls (Fig. 1). The experimental cell is placed into thermostat. The resistance has been determined by alternating current with the frequency 80 MHz.

The measured resistance has the contributions from polarization of the sample and electrodes. To exclude the electrode contribution the measurements have been performed for different pairs of electrodes: 1 and 3, 2 and 3 (Fig. 1). The resistance in this case may be presented as follows:

$$R_{13} = \frac{l_{13}}{\pi r^2 \sigma} + R_{\text{Pt}} + R_{\text{W}}; \quad (1)$$

$$R_{23} = \frac{l_{23}}{\pi r^2 \sigma} + R_{\text{Pt}} + R_{\text{W}}; \quad (2)$$

where  $R_{13}$  and  $R_{23}$  are measured resistances between electrodes 1 and 3, 2 and 3, respectively;  $l_{13}$  and  $l_{23}$  are the distances between electrodes 1-3 and 2-3, respectively;  $r$  is the capillary radius;  $\sigma$  is the specific conductance,  $R_{\text{Pt}}$  and  $R_{\text{W}}$  are the resistances of platinum and wolfram electrodes, respectively. The first terms in equations (1) and (2) describe the resistance of the sample, while the second and the third terms describe the polarization resistance of electrodes.

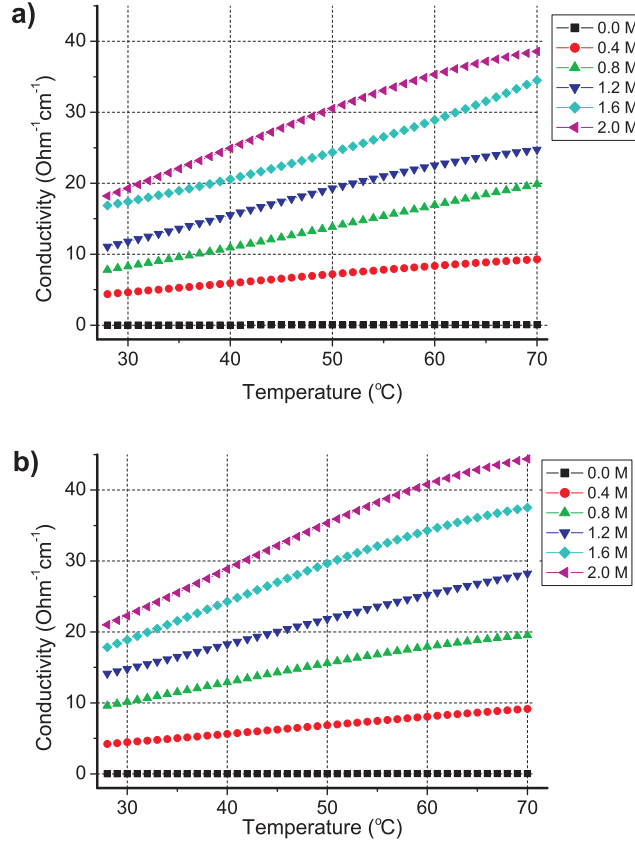


Figure 2: Temperature dependence of electrical conductivity of the samples. a) DNA solution with added KCl salt. b) KCl solution.

The difference of formulae (1) and (2) gives the following formula for conductivity of the sample:

$$\sigma = \frac{l_{12}}{\pi r^2 (R_{13} - R_{23})}, \quad (3)$$

where  $l_{12}$  is the distances between electrodes 1-2. Using the formula (3) the conductivity of the samples are determined.

### 3 Results

The temperature dependences of electrical conductivity of salt solution ( $\sigma_{\text{KCl}}$ ) and solutions of DNA with added salt ( $\sigma_{\text{DNA+salt}}$ ) are obtained (Fig. 2). The results show that the conductivity of the samples increases as the temperature increases for all considered samples.

According to the activation mechanism of ion motion in the solution the temperature dependence of conductivity of the system may be considered analogically to the Arrhenius equation for the temperature dependence of chemical reaction rates [37]:

$$\sigma = \sigma_0 \exp \left( -\frac{\Delta E}{k_B T} \right), \quad (4)$$

where  $\sigma_0$  is the coefficient;  $\Delta E$  is the potential barrier;  $k_B$  is the Boltzmann constant;  $T$  is the temperature. The exponent describes the probability of ionic jumping over the potential

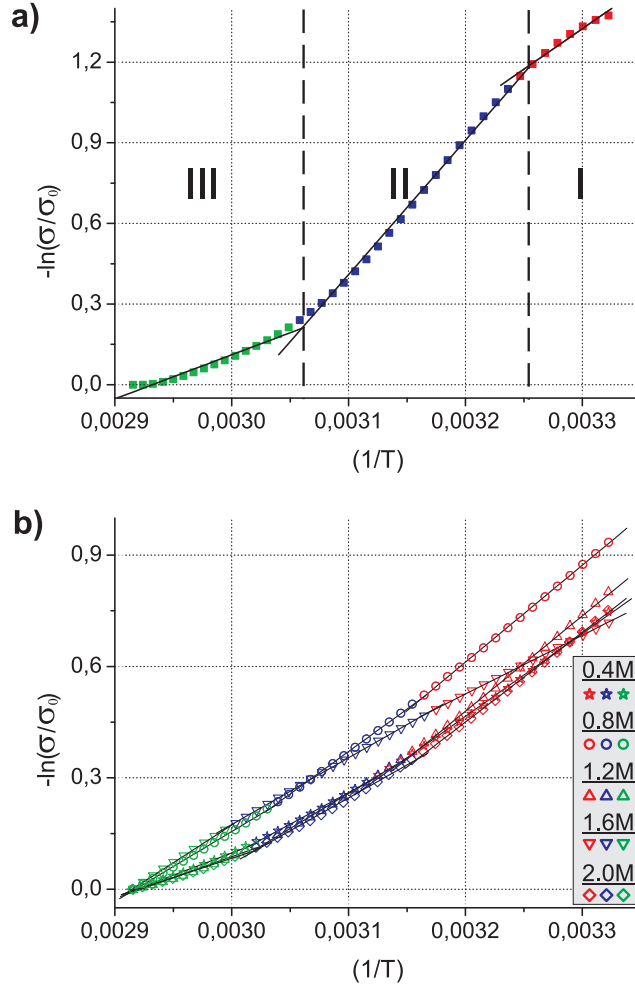


Figure 3: The Arrhenius plot for DNA water solutions. a) Salt free solution. I is range of double-stranded DNA (red points); II is transition range of double helix melting (blue points); III is range of single-stranded DNA (green points). b) Solution of DNA with added salt. Solid black lines is the linear approximation.

barrier due to the thermal fluctuations. To analyze the temperature dependence of electrical conductivity let us use the Arrhenius coordinates, describing the logarithm of conductivity as the function of transverse temperature. From formula (4) it is seen that the temperature dependence of conductivity in Arrhenius coordinates should be linear.

The Arrhenius plot for salt free solution of DNA (Fig. 3a) shows that there are two braking points separating distinguishable linear ranges. Linear ranges in the Arrhenius plot characterize melting process of DNA double helix [18]. The range I ( $28 \div 37$  °C) and III ( $54 \div 70$  °C) features the double stranded and single-stranded DNA, respectively. The range II ( $37 \div 54$  °C) characterizes denaturation of DNA macromolecules. In case of DNA with added salt the difference between linear ranges in the Arrhenius plot is not prominent and braking points are hardly distinguishable (Fig. 3b). The influence of added salt may be explained by additional neutralization of the negatively charged atomic groups of the double helix by salt ions.

Different ranges in Arrhenius plot characterizes different activation energy of ionic motion in the solution. The values of potential barrier  $\Delta E$  are determined as a slope of the lines in Fig. 3

Table 1: Values of potential barrier  $\Delta E$  for the ion motion in DNA solution (kJ/mole).

	0 M	0.4 M	0.8 M	1.2 M	1.6 M	2.0 M	Mean
I	25.01	18.55	21.71	21.33	13.15	20.10	$19 \pm 4$
II	41.52	14.07	18.99	15.78	14.90	14.74	$16 \pm 2$
III	13.62	9.98	15.65	9.36	16.83	8.61	$12 \pm 4$
							$16 \pm 4$

(Table 1). The results show that in salt free solution of DNA before the melting temperature (range I) the activation energy is rather large comparing to the electrolyte solution (about 25 kJ/mole). In the transition range (range II) the activation energy (about 43 kJ/mole) increases almost twice comparing to the range I that is effectively caused by the ejection of counterions from DNA ion-hydrate shell [9]. Under the melting temperatures (range III)  $\Delta E$  values decrease.

In the solutions of DNA with added salt the potential barriers  $\Delta E$  of different ranges are rather close. Comparing to the salt free solution  $\Delta E$  values only slightly decrease in case of the range I and range III, while in case of the range II it decrease more than twice. The fact of comparatively low activation barrier in the range II indicates that the added salt increases the melting temperature of DNA double helix that is also observed in calorimetric experiments [2].

Increasing the concentration of added salt the conductivity of the both DNA solution and electrolyte increases (Fig. 2). To compare the conductivity of DNA solution with added salt and the conductivity of KCl electrolyte solution the difference  $\Delta\sigma = \sigma_{\text{DNA+KCl}} - \sigma_{\text{KCl}}$  is analyzed (Fig. 4). The results show that at concentrations lower than some critical one (about  $c_{\text{cr}} \approx 0.4$  M) the conductivity of DNA solution is higher than the conductivity of salt solution ( $\sigma_{\text{DNA+salt}} > \sigma_{\text{salt}}$ ). Under the critical concentration ( $c = c_{\text{cr}}$ ) the conductivity of DNA solution and KCl solution are equal ( $\Delta\sigma = 0$ ). Starting from critical concentration ( $c > c_{\text{cr}}$ ) the conductivity of DNA solution is lower than the conductivity of respective electrolyte ( $\sigma_{\text{DNA+salt}} < \sigma_{\text{salt}}$ ).

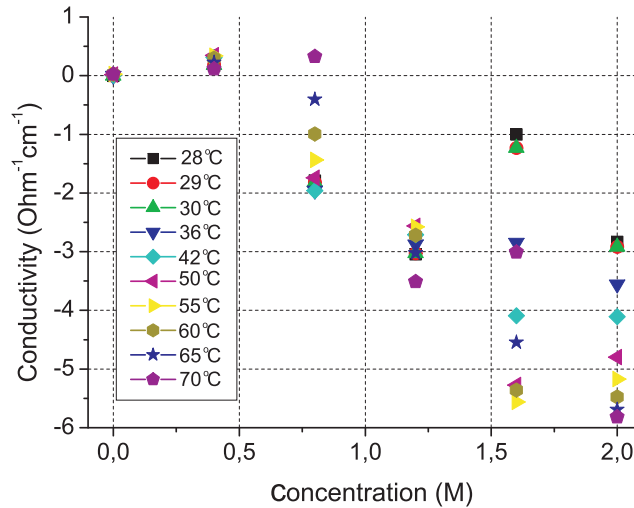


Figure 4: Concentration dependence for difference between conductivities of DNA and electrolyte solutions.

The dependence of conductivity of DNA solution on salt concentration at range from 0 to  $c_{\text{cr}}$  is about the same for different temperatures, while at the concentration range from  $c_{\text{cr}}$  to 2 M it is different for different temperatures. The changes of  $\Delta\sigma$  values should reflect the structure changes in DNA solution.

## 4 Model

To understand the mechanism of electrical conductance of DNA water solution let us analyze the state of DNA macromolecule in the solution. Due to the large contour length DNA macromolecules are coiled shaped. The size of DNA coils may be estimated with the use of the persistence model [2, 38]. In framework of this model the root-mean-square distance between the ends of macromolecule is determined as follows:

$$\bar{D}^2 = 2P^2(L/P - 1 + e^{-L/P}), \quad (5)$$

where  $L$  and  $P$  are the contour and persistence lengths of macromolecule, respectively. The contour length for DNA from salmon testes is  $L \approx 0.68 \mu\text{m}$  [36]. The persistence length of DNA is  $P \approx 500 \text{ \AA}$  [3, 36]. Using such parameters the average volume of DNA coils is estimated  $0.02 \mu\text{m}^3$ . Taking into consideration that average number of DNA macromolecules in 1 ml of the experimental solution is  $10^{15}$  the total volume of DNA coils should be about 20 ml. One can conclude that macromolecule coils overlap in the considered solution and the conductivity process may be determined by mobile ions only, because the migration of single DNA macromolecules is labored.

The number of mobile ions involved in conductivity process is determined by the concentration of DNA counterions and ions of added salt. Taking this into consideration the conductivity of DNA solution may be presented as follows:

$$\sigma_{\text{DNA+salt}}(c) = \sigma_1(c) + \sigma_2(c), \quad (6)$$

where  $\sigma_1(c)$  is the conductivity determined by the motion of salt ions (bulk ions);  $\sigma_2(c)$  is the conductivity determined by mobility of counterions in ion-hydrate shell of DNA;  $c$  is the equivalent concentration of added salt.

Taking into consideration that salt ions may condense on DNA macromolecule the conductivity of bulk ions may be considered as follows:

$$\sigma_1(c) = \sigma_{\text{salt}}(c) - A_1(c)(\lambda^+ + \lambda^-), \quad (7)$$

where  $\sigma_{\text{salt}}(c)$  is the contribution of salt ions to the conductivity of the system;  $A_1(c)$  is the concentration of salt ions condensed on DNA macromolecule;  $\lambda^+$  and  $\lambda^-$  are equivalent mobility of positively and negatively charged ions, respectively. The second term in (7) describes the conductivity decrease caused by the association of the positively and negatively charged ions with DNA. Note that the negatively charged ions may associate with the positively charged ions that are already tethered to the phosphate groups of DNA backbone.

The contribution from DNA counterions to the conductivity of the system may be taken into consideration as follows:

$$\sigma_2(c) = c_p \lambda^+ - A_2(c) \lambda^+, \quad (8)$$

where  $c_p$  is the concentration of DNA counterions that approximately equals to the number of DNA phosphate groups;  $A_2(c)$  is the concentration of counterions associated with the negatively

charged atomic groups of DNA macromolecule. The first term in (8) describes the contribution from DNA counterions to the conductivity of the system. The second term in (8) describes the conductivity loss caused by the association of counterions with the phosphate groups of DNA macromolecule. Taking into account the formulae (6), (7) and (8) the contribution of DNA to the conductivity of polyelectrolyte solution ( $\Delta\sigma = \sigma_{\text{DNA+salt}} - \sigma_{\text{salt}}$ ) may be determined as follows:

$$\Delta\sigma = c_p\lambda^+ - A_2(c)\lambda^+ - A_1(c)(\lambda^+ + \lambda^-). \quad (9)$$

The concentration of condensed ions may be considered proportional to the concentration of salt and concentration of DNA phosphate groups, respectively:  $A_1(c) = \beta(c)c$  and  $A_2(c) = \alpha(c)c_p$ . The coefficients  $\alpha(c)$  and  $\beta(c)$  depend on concentration of added salt and describe the part of the ions condensed on macromolecule surface. Let us consider the functions  $\alpha(c)$  and  $\beta(c)$  in linear approximation:

$$\alpha(c) = \alpha_0 + \alpha_1 c; \quad \beta(c) = \beta_0 + \beta_1 c, \quad (10)$$

where  $\alpha_0$ ,  $\alpha_1$ ,  $\beta_0$  and  $\beta_1$  are the parameters that may be determined from the following conditions.

In case of salt free solution ( $c = 0$ ) the conductivity is determined by free counterions of DNA and  $\alpha|_{c=0} = 0$ , thus  $\alpha_0 = 0$ . Increasing salt concentration the degree of neutralization of DNA surface increases, and under some concentration point ( $c = c_{\text{cr}}$ ) all phosphate groups of the double helix become neutralized. Since the counterions, attached to DNA macromolecule, are not involved in the conductivity process the condition  $\alpha|_{c \geq c_{\text{cr}}} = 1$  should be valid, thus  $\alpha_1 = 1/c_{\text{cr}}$ . The ions of added salt condense on counterions that are already tethered to the phosphate groups of DNA backbone, therefore  $\beta|_{c \leq c_{\text{cr}}} = 0$ , and  $\beta_0 = -\beta_1 c_{\text{cr}}$ . Further increase of salt concentration leads to the crystallization of salt ions, and under some defined concentration ( $c = c_{\text{max}}$ ) the crystallization will be maximal that corresponds to the condition  $\beta|_{c=c_{\text{max}}} = 1$ , and  $\beta_1 = 1/(c_{\text{max}} - c_{\text{cr}})$ . Taking into consideration these conditions the formulae (10) may be written in the following form:

$$\alpha(c) = \frac{c}{c_{\text{cr}}}; \quad \beta(c) = \frac{c - c_{\text{cr}}}{c_{\text{max}} - c_{\text{cr}}}. \quad (11)$$

The temperature dependence of ion mobility may be taken into consideration analogically to the equation (4):  $\lambda = \lambda_0 \exp(-\Delta E/k_B T)$ , where  $\lambda_0$  is the characteristic equivalent mobility. The value of  $\lambda_0$  may be determined using known values of ion mobility for some defined temperature  $T_0$ :  $\lambda_0 = \lambda(T_0) \exp(\Delta E/k_B T_0)$ . Taking this into consideration, and substituting the formulae (11) to the equation (9), the formula for  $\Delta\sigma$  may be written in the following form:

$$\Delta\sigma = \begin{cases} \frac{(c_{\text{cr}}-c)c_p\lambda_0^+}{c_{\text{cr}}} \exp\left[-\frac{\Delta E(1-T/T_0)}{k_B T}\right], & c \leq c_{\text{cr}}; \\ -\frac{(c-c_{\text{cr}})c(\lambda_0^+ + \lambda_0^-)}{c_{\text{max}} - c_{\text{cr}}} \exp\left[-\frac{\Delta E(1-T/T_0)}{k_B T}\right], & c > c_{\text{cr}}. \end{cases}$$

In the equation (12)  $\lambda_0^+$  and  $\lambda_0^-$  are the mobility of positively and negatively charged ions under characteristic temperature  $T_0$ .

It is seen that  $\Delta\sigma$  values are positive under the salt concentration range  $c \leq c_{\text{cr}}$ . In case of high concentrations of added salt ( $c > c_{\text{cr}}$ ) the values  $\Delta\sigma$  are negative. The contribution of DNA to the conductivity of polyelectrolyte is inessential ( $\Delta\sigma = 0$ ) when all phosphate groups of DNA backbone are neutralized ( $c = c_{\text{cr}}$ ). Note the developed model does not take into consideration the degradation process of DNA macromolecules under the melting temperatures.



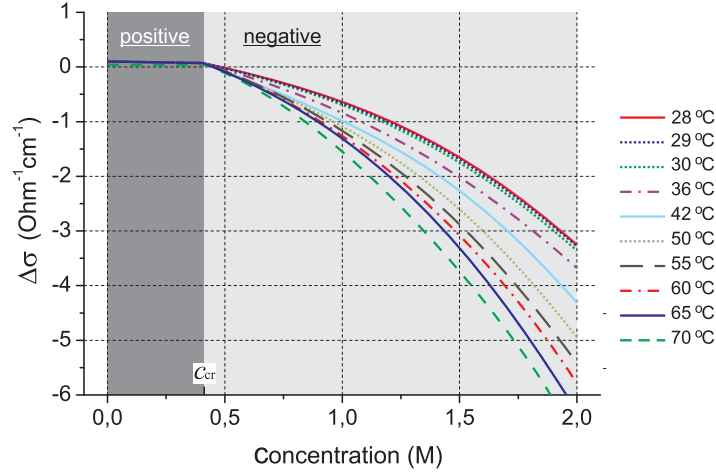


Figure 5: Concentration dependence for the difference between conductivity of DNA and of electrolyte solution on salt concentration, calculated by the formula (12).

## 5 Discussion

To characterize the influence of DNA macromolecules on conductivity of the system let us estimate  $\Delta\sigma$  by formula (12). The parameters, necessary for the calculations, are determined as follows. The concentration of phosphate groups in solution is determined according to the concentration of DNA in the experimental samples (2 mg/ml)  $c_p = 6.35$  M. The maximal salt concentration is taken the same as solubility limit of KCl  $c_{\max} = 4.6$  M [39]. The value of critical concentration of added salt  $c_{\text{cr}} = 0.4$  M is determined from the condition  $\Delta\sigma = 0$ . The characteristic mobility  $\lambda_0^+$  and  $\lambda_0^-$  for  $\text{K}^+$  and  $\text{Cl}^-$  ions are taken the same as in electrolyte solution  $\lambda_0^+ = 55.1 \text{ cm}^2\Omega^{-1}\text{mole}^{-1}$  and  $\lambda_0^- = 55.8 \text{ cm}^2\Omega^{-1}\text{mole}^{-1}$  under the temperature  $25^\circ\text{C}$  [37]. The potential barrier  $\Delta E \approx 16 \text{ kJ/mole}$  is taken as average value of activation energies (Table 1). As the result the concentration dependences of  $\Delta\sigma$  are shown in Figure 5.

It is seen that the conductivity of DNA solution in concentration range  $c < c_{\text{cr}}$  is practically the same as the conductivity of respective electrolyte solution, and  $\Delta\sigma$  is positive. At higher concentrations ( $c > c_{\text{cr}}$ ) the obtained difference between conductivity of DNA solution and electrolyte solution is negative. Increasing the temperature, the values of  $\Delta\sigma$  decrease in this concentration range. The calculated results (Figure 5) qualitatively agree with the experimental data (Figure 4). However, in the concentration range  $c < c_{\text{cr}}$  the experimentally observed values of  $\Delta\sigma$  are larger, which may be caused by complexity of the mechanism of counterion condensation on DNA.

According to the results of estimations the following mechanism of counterion ordering around DNA macromolecules may be introduced. Under the low concentration of added salt the degree of phosphate group neutralization is about the same as in the case of salt free solution (Figure 6a). The counterions come off the ion-hydrate shell of macromolecule and determine the conductivity of the system. Increasing salt concentration the number of neutralized phosphate groups increases and under the critical concentration the phosphate groups should be completely neutralized (Figure 6b). The counterions with the phosphate groups form electrically neutral system resembling to the lattice of ionic crystal (ion-phosphate lattice) [30–33]. The formation of DNA ion-phosphate lattice induces the decrease of conductivity of the system. After the formation of ion-phosphate lattice salt ions condense on counterions tethered to the phosphate

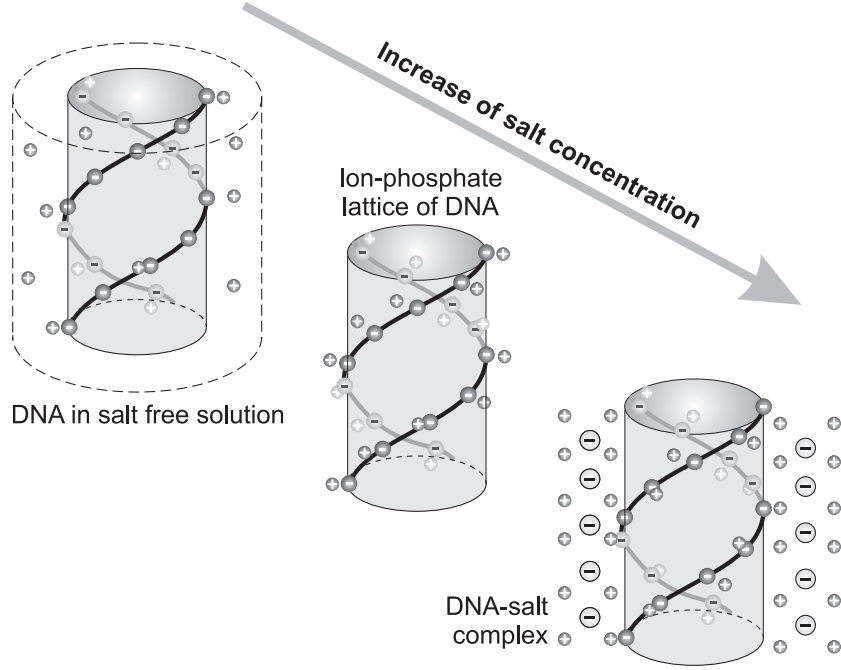


Figure 6: Scheme of the process of ionic structuring around DNA double helix at different concentrations of added salt.

groups of macromolecule, and DNA-salt complexes are formed (Figure 6c). Such complexes may be observed as the textures on a surface after evaporation of solution [16]. Formation of DNA-salt complexes reduces the conductivity of the system due to the decrease of the number of positively and negatively charged ions involved in the electric current.

## 6 Conclusions

In the present work the ordering of ions in DNA water solutions is studied by conductivity experiments. As the result the temperature dependence (from 28 to 70  $^{\circ}\text{C}$ ) of conductivity for DNA solution with KCl salt (the concentration from 0 to 2 M) are obtained. In case of salt free solution there exist three characteristic temperature ranges describing the stages of the melting process of DNA double helix. In case of DNA with added salt the characteristic stages of DNA melting are hardly distinguishable that may be due to the stabilization of the double helix by the ions of added salt. The comparison between conductivity of DNA solution with the added salt and electrolyte solution shows that under the concentrations lower than 0.4 M (critical concentration) the conductivity of DNA solution is higher than the conductivity of respective electrolyte. Starting from the critical concentration the conductivity of electrolyte is higher than the conductivity of DNA solution.

Basing on developed phenomenological model for the conductivity of DNA solution, the mechanism of ionic ordering in DNA solution is introduced. It is considered that under the low concentrations of added salt DNA counterions do essential contribution to the electrical conductivity of the system. Increasing salt concentration to the critical one the counterions condense on DNA macromolecule and the ion-phosphate lattice is formed. Further increase of salt concentration leads to the condensation of anions on cations attached to the phosphate groups

of DNA backbone and DNA-salt complexes are formed. Growth of the DNA-salt complexes decreases the conductivity of the system. The introduced mechanism qualitatively describes the experimentally observed changes of conductivity of DNA solutions.

## 7 Acknowledgements

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